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ENTROPY AND TEMPERATURE

by

Oscar Biblarz

December 1972

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# NAVAL POSTGRADUATE SCHOOL Monterey, California

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#### ABSTRACT

This article is written in the style of Scientific American. A minimum of mathematics is used in the presentation of a new approach to the understanding of the second law of thermodynamics. The intended readers are engineering students who have been exposed to a standard version of undergraduate thermodynamics (such as AE 2041). It is shown here that, by extending the use of entropy and temperature to nonequilibrium situations, a more complete formulation of the second law is possible. Applications of the foregoing concept to fluid flow, chemical reactions, and lasers are presented.



#### ENTROPY AND TEMPERATURE

by

#### Oscar Biblarz

By assuming that for a system in internal thermal nonequilibrium there exists a temperature as well as an entropy, we can develop some results from the Second Law of Thermodynamics in a less esoteric fashion.

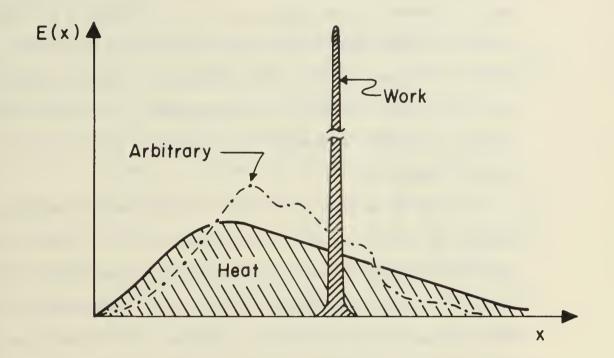
#### Introduction

Beginning students in thermodynamics usually find that understanding how to use the First Law is largely a matter of common sense -- somehow, energy is always conserved. Energy changes must be balanced by accounting for energy in transit as either work or heat. While the exact distinction between work and heat may be somewhat elusive at first, the novice can usually develop an intuition which helps him recognize the distinction. What often helps drive home the difference is the fact that purchasing energy in the form of work is more expensive than an equal amount in the form of heat. When thermodynamics is presented in terms of microscopic concepts, work is described as ordered energy transfer, and heat as transfer of energy which is in a state of maximum disorder. Order, then, is more expensive in nature. The beauty of the First Law is that its understanding can become intuitive; it is good for equilibrium and nonequilibrium situations (since an energy balance is always involved); and, it is universal. The accounting scheme is so basic to our scientific thinking that it seems unnecessary to emphasize its importance.

Now when beginning students face the Second Law, an entirely different situation arises. They are forced to deal with inequalities

and highly idealized situations which result in the level of abstraction increasing astronomically. The question then arises as to where these complications come from. Why must the balancing scheme be abandoned? The answer seems to be that these abstractions derive from our insistence in dealing with equilibrium states instead of the more general (and more realistic) nonequilibrium situations. The world of strict equilibrium is a very dull one because nothing can happen. Yet, thermodynamics has been a very useful science because somehow we manage to let systems at different equilibrium states interact.

In this article it is proposed that a system in internal thermal nonequilibrium be described by "extended" parameters which allow a complete formulation of the Second Law. The extension requires the assumption of a relationship between entropy and temperature which is not only consistent with the concept of state of thermodynamics, but which also accounts for nonequilibrium situations. A system in internal thermal nonequilibrium is not describable by a single temperature, so we usually resort to breaking up the system into subsystems each of which may be assigned an equilibrium value of the temperature. For example, this is what is done in heat transfer. However, it will be useful here to describe the nonequilibrium situation with one parameter corresponding to the temperature and one corresponding to the entropy. These may be defined by a curve which represents the distribution or spectrum of the energy (see the illustration on page 3 (Fig 1)). It will be clarified later that analytical statements for the spectrum of the system energy can only be obtained for the two extreme cases, namely, heat (complete randomness) and work (complete order). Anything in between would likely require the use of empirical information. This apparent drawback should not detract from the utility of the approach since we can show the usefulness of the nonequilibrium



X denotes the variable on which the spectral energy depends, i.e., velocity, frequency or wavelength, etc. The area under each curve would be the same if the total energy represented by each is the same. This spectral representation is most common for electromagnetic radiation as shown in the illustration on page 22 (Figure 8)

FIGURE 1

parameters in deriving conclusions from the Second Law. For example, this method of analysis should account for the balancing of heat and work and any combination of the two; it should show what happens when work is degraded to heat, and so on. We note in passing that the inequality in the usual entropy formulations arises solely from irreversible changes so that these formulations always go beyond the stated equilibrium limitation of thermodynamics. If we have allowed the entropy to represent a nonequilibrium situation, why can't we do the same with the temperature?

In order to motivate an intrinsic relation between temperature and entropy, we have to resort to the microscopic point of view of thermodynamics which hinges on the assumption that the behavior of matter can be described through the aggregate behavior of its fundamental particles. These fundamental particles may be molecules (as in a gas), electrons and ions (as in a plasma), or photons (as in electromagnetic radiation). The aggregate behavior of these particles is formulated using statistics because there are so many particles and because in the microscopic world the behavior of these particles is postulated to be random [see "Probability" by M. Kac, Scientific American, September, 1964]. We say that the particles individually obey the laws of mechanics (or more precisely quantum mechanics) so let's recall what some of the elementary concepts from ordinary mechanics tell us about energy. If a projectile, such as a baseball, is traveling through space with some known velocity, then its energy is given by the sum of its kinetic and potential energies. We would not be interested in the internal (thermal) energy unless the projectile were to change temperature. Although we feel confident that we could measure this temperature with a suitable thermometer, there is no hint from mechanics of how temperature enters into the problem. There

is similarly no hint of the concept of entropy. Moreover, while the First Law of thermodynamics recognizes the existence of nonmechanical forms of energy, this law gives no insight into the nature of either temperature or entropy.

But what is the temperature of a fundamental particle? Since fundamental particles follow the laws of mechanics, we much conclude that a fundamental particle has an energy but that it does not have a temperature (or that it would be redundant to introduce the idea of temperature). Similarly, a fundamental particle has no entropy. In microscopic thermodynamics it is shown that a <u>vast</u> number of fundamental particles has an energy, a temperature, and an entropy (at equilibrium). Elegant equations are available to describe the interrelationships between these properties. In fact, the concept of state tells us that for a single component substance in a single state (i.e., gas, liquid, or solid), if we know two properties, we have automatically defined any other. That is, knowing the temperature and the entropy we are able to know what the energy is. The thing to note is that since energy changes must always be accountable, there should exist nonequilibrium temperatures as well as entropies provided the concept of state holds.

We see then that the nature of temperature and entropy somehow must be connected with vast collections of fundamental particles. For example, to illustrate an everyday situation, let us say that we have a gas in a container and that this system is totally isolated from the surroundings. To this gas we ordinarily attribute an energy, a volume, and a pressure. We can easily measure volume and pressure. Now, from a microscopic viewpoint, the pressure arises from collisions of gas molecules with the walls since they are at continuous random motion by virtue of their nonzero energy. Volume and pressure are intuitive enough, but we observe

that pressure is also a result of this aggregate behavior of elementary particles and that if the distribution of particle energies changes, the pressure should also change. The thermal energy is calculated via the temperature of the gas. Temperature is certainly a measurable property, however, we need to resort to the so-called Zeroth Law of thermodynamics to "license" thermometry and to the Second Law to argue that the measured temperature is independent of the measuring substance (just as volume is independent of the material in the yardstick we use).

There is no satisfactory way to measure entropy; yet, we know it to be an index of disorder for the fundamental particles. A system at equilibrium is said to have its constituent particles in a state of maximum disorder. Entropy is a maximum at equilibrium and, for a fixed quantity of energy, takes smaller and smaller values for varying degrees of internal nonequilibrium.

#### Nonequilibrium

The methodology of basic thermodynamics carefully avoids nonequilibrium situations. Heat transfer is treated as occurring across a vanishingly small temperature difference even though this is clearly impossible in real life! The principal reason for wanting to stick to equilibrium changes is that they are reversible, i.e., if there were no nonequilibrium, there would be no irreversibilities. This is true in thermal as well as mechanical and chemical changes. In fact, the nonequilibrium situation is synonymous with the ability of a system to perform some work and this is an important observation. Any departure of a system, internal or external, from equilibrium indicates the potential of that system to exchange work. In the case of thermal nonequilibrium we may place a Carnot engine across the temperature difference to carry out any reversible change we desire (at least on paper).

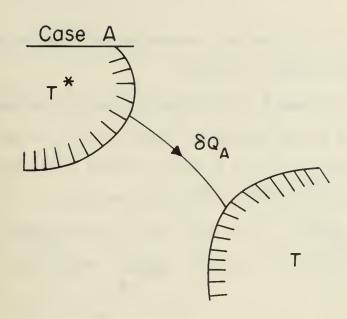
What, then, is an irreversibility? An irreversibility results from the partial or total inability of a system to accomplish this work which potentially exists by virtue of the nonequilibrium present. Irreversibility, then, denotes the strong tendency of nature towards disorder. In thermodynamics we usually explain irreversibility in terms of reversibility. The latter concept says that if you could retrace the steps of a process and thereby cause everything to return to its original state, then the process is reversible. That is, if you walk down the beach and then walk backwards, your footprints will erase themselves. Not only that, but you will not be tired at all! Clearly, natural processes are irreversible. The interesting thing is that the motion of the individual particles in the microscopic world may be considered to be reversible, but since their behavior is random or uncorrelated, the aggregate behavior of the fundamental particles exhibits irreversibilities. The change is overwhelmingly from order to disorder.

A Carnot engine is an ideal cycle which treats reversibly an external thermal nonequilibrium. Because it is completely reversible, the Carnot engine is thermally the most efficient. The Carnot engine is a useful tool for thermodynamic analysis because it permits us to deal with thermal nonequilibrium. Let us illustrate next what all of this says regarding heat transfer across a finite (large) temperature difference. As it is usual in this field, we will deal with infinitestimal or differential quantities of energy transfer so that the heat transfer will not appreciably change the temperatures involved. Suffice it to say, any conclusion drawn from an analysis using infinitestimal quantities is valid for finite quantities.

Consider a system in internal thermal nonequilibrium and focus on two small subsystems which can be identified with equilibrium parameters. Suppose that we investigate the heat transfer between the two subsystems, one at a temperature T\* and the other at a lower temperature T. We say that the total change of entropy for the system is greater than zero because the process is irreversible. Consider two cases, one where a small quantity of heat flows directly across this large temperature difference (Case A), and the other where we put a Carnot engine between the two reservoirs (Case B). These cases are shown on the illustration on page 9 (Figure 2).

Now, let us look at the case where we insert the Carnot engine between the two reservoirs; the engine receives the same quantity of heat  $\&Q_A$  from the high temperature reservoir and rejects a smaller quantity of heat  $\&Q_B$  to the low temperature reservoir. Simultaneously, a quantity of work  $\&Q_B$  is produced. This is shown on the bottom illustration on page 9 (Figure 2).

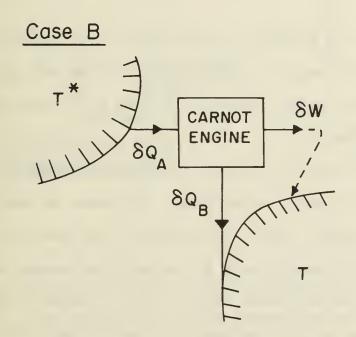
Since the change (dS)\* of the entropy of the high temperature reservoir is the same in both cases and since the change of entropy of the Carnot engine is zero (by definition of a cycle), then we have succeeded in isolating the irreversibility to the low temperature reservoir. If we add the quantity of energy represented by  $\delta Q_A$  to the low temperature reservoir entirely as heat, then the overall change of entropy is shown to be greater than zero. However, if we add this energy as  $\delta Q_B$  plus  $\delta W$ , then the overall change of entropy is zero. So we may say that in Case A not converting some heat to work makes the process irreversible. Similarly, if we now change  $\delta W$  into an equivalent amount of heat in Case B, the process will include an irreversible transformation. We have shown



$$dS_{A} = dS^{*} + dS$$

$$= -\frac{\delta Q_{A}}{T^{*}} + \frac{\delta Q_{A}}{T}$$
since  $T^{*} > T$ 

$$dS_{A} > 0$$



 $\delta Q_A = \delta Q_B + \delta W$ ,

But  $dS_B = O$ since the presence of the Carnot

Engine makes the entire process reversible

$$dS^* = -\frac{\delta Q_A}{T^*} = dS_A - \frac{\delta Q_A}{T} = -\frac{\delta Q_B}{T}$$
Therefore,  $T dS_A = \delta Q_A - \delta Q_B$ 

$$= \delta W$$
or  $T dS_A = \delta (W \longrightarrow Q) > 0$ 

Differential amounts of heat and work are denoted by  $\delta(\cdot)$  because they are path functions in contrast to entropy which is a point function and its differential amount is denoted by  $d(\cdot)$ .

that the overall irreversibility of the heat transfer arises from the nonequilibrium quantity of energy, namely, the work.

The last equation shown on page q is appealing because TdS represents an energy and so does  $\delta W$ , and we may balance the equation since the two quantities are equal. The important thing to recall is that in the overall (isolated) system a certain ability to do work has been lost. Energetically, the equation shown at the bottom of the illustration on page 9 (Figure 2) holds, in which the inequality sign in conspicuously absent.

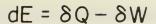
#### Postulate

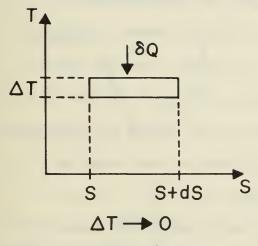
Consider the transfer of energy to a closed system. This transfer may take place as either heat or work, or as a combination of the two. This is what the First Law tells us, namely, the equation shown at the top of the illustration on page 11 (Figure 3).

We can use the Carnot engine to visualize how these two modes of energy transfer may be individually accomplished. Of course, we have already discussed heat transfer, and it will suffice to say that if we make the temperature difference go to zero across the Carnot engine then we perform conceptually reversible heat transfer. This is shown in the temperature-entropy diagram on the illustration on page 11 (Figure 3). Now, work transfer could be visualized as a Carnot engine operating between two reservoirs with small amounts of heat transferred. The larger the temperature difference, the better. So we may summarize the preceding ideas for infinitestimal processes as follows:

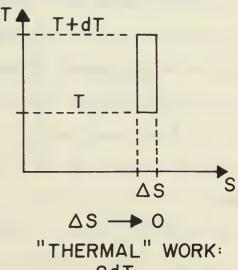
reversible heat transfer: TdS "thermal" work: SdT

Since a given amount of energy transfer may consist of some work and some heat transfer, it is logical that the transfer of energy be





REVERSIBLE HEAT TRANSFER: TdS



SdT

The sign convention for the First Law says that heat is positive into the system whereas work is positive out of the system.

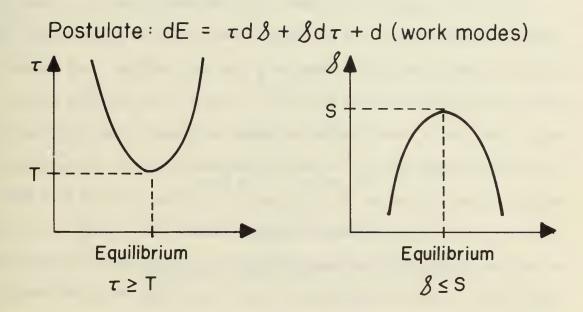
FIGURE 3

represented by the sum of the two quantities above. A problem arises, however, from the fact that work implies nonequilibrium and T and S are defined strictly for equilibrium! So, we proceed to postulate here a relationship for the total energy transfer which is shown in the illustration on page 13 (Figure 4), where  $\tau$  and  $\mathcal{J}$  are nonequilibrium parameters with characteristics depicted in the same illustration.

The postulated equation should be valid for equilibrium or nonequilibrium transfers of energy since we aim to present a complete expression for the energy. Moreover, we can observe from the right-hand side of the equation in the illustration on page 13 (Figure 4) that for a fixed energy change, the effects on d<sub>T</sub> and d<sub>A</sub> are symmetrical as we go from nonequilibrium to equilibrium when no work modes are present.

We may refer to T as a "temperature" which may be associated with a distribution of thermal energy which is less than completely random. By necessity, the smaller the spectrum of the total energy the higher the curve must peak, i.e., the higher the effective temperature (see illustration on page 3 (Figure 1)). We shall see this in the last section of this paper where electromagnetic radiation is treated (as an example). Clearly, if we have a number of fundamental particles at precisely the same energy and in phase, we can do such things as move a piston by virtue of an exchange of the particle energy with the piston (i.e., we can do work!).

We noticed in the introduction that when the temperature is altered, because of a nonequilibrium situation, the entropy will similarly be affected. A less than completely random distribution means a smaller entropy (since it measures disorder) and, hence,  $\mathcal J$  is really the entropy



Postulate for the complete representation of the change of energy due to heat and work transfers in terms of the extended parameters for temperature and entropy.

FIGURE 4

whose usage transcends its definition. In fact, either the Boltzmann or the Gibbs relation precisely describe the entropy in either equilibrium or nonequilibrium through the thermodynamic probability concept. However, any discussion of these formulas is too lengthy for this article.

Let us now apply the postulate to an isolated system in a state of internal nonequilibrium. By isolated we mean that the system under study does not exchange energy (or mass) with its surroundings. Any process that occurs in nature may be described in terms of an isolated system because the system specification is always arbitrary. The importance of the isolated system lies in a powerful generalization in thermodynamics which says that in nature the direction of a process must be such that the entropy will (most probably) increase during this process. Of course, we must presuppose that the system changes due to an initial nonequilibrium state which is able to equilibrate. Since the change of system energy is zero it can be shown (see the illustration on page 15 (Figure 5)) that the increase of entropy is a reflection of the decrease of "temperature" or the loss of the thermal work. This result represents a statement of the Second Law. Since the entropy can only increase in this case (no heat transfer), one could argue that our methodology appears circular. Taken as a proof or merely as a check, our definition of the behavior of T is consistent with the Second Law. The reader may have recognized that the principle of the increase of entropy is the basis for the prediction of the eventual "thermal death" of the universe.

#### Lost Work

Isolated System

The deterioration of mechanical energy into internal thermal energy is a familiar event. The brakes of an automobile do precisely this; it is simply cheaper to dissipate the car's kinetic energy than to recover

 $\tau d A + \Delta d\tau = 0$ 

та **/** = - **/** ат

or  $d \lambda > 0$  since  $d\tau < 0$ 

and  $\lambda$  and  $\tau$  are positive

( $\tau$  and  $\boldsymbol{J}$ denote nonequilibrium parameters)

FIGURE 5

it. Other everyday examples can be mentioned such as the stirring of a liquid or frictional losses in a fluid flowing through a long duct. In this last example the Second Law is usually balanced by the inclusion of a term called "lost work." That is, the temperature times the change of entropy equals the heat transfer plus the lost work. Such an equation is perhaps of limited usefulness because the losses must be determined experimentally. The lost-work term is always positive unless the process is reversible whereupon it is zero.

As long as all of the work is going to be dissipated, it is possible to think of a mechanical work input into a system as heat energy coming from a very high (i.e., infinite) temperature source. This is because, while heat exchange ceases when the lower temperature rises to equal the source temperature, work may continue to be absorbed by the system no matter how high its temperature gets to be. We can see, therefore, that defining a thermal work term as AdT can be quite useful.

The complexity of the phenomena involved in the transformation of mechanical energy into internal thermal energy of a fluid is nowhere more apparent than in turbulence. Turbulence corresponds to an incomplete deterioration of fluid dynamic energy (i.e., the entropy is not a maximum) which represents varying degrees of nonequilibrium (see the illustration on page 17 (Figure 6)). In fluids of very low viscosities, such as air and water, friction in the molecular sense is very slow in dissipating mechanical energy so nature apparently resorts to random behavior on a large scale to speed up the process. The formation of turbulent eddies represents a particularly effective shortcut in the dissipation of mechanical energy. The spectrum of turbulence varies from case to case and is observable in nature in practically every flow situation. Turbulence governs











(disorder)

FIGURE 6

ORDER -TURBIJEE

atmospheric phenomena, mixing phenomena (of importance in the dispersion of pollutants), etc.

#### Thermodynamic Potentials

Another important case that may be easily treated here is that of a chemical reaction where no mass is exchanged with the environment but where heat is transferred. There are two common cases of interest, namely, a constant volume chemical reaction and a constant pressure reaction. In the former case, the reacting chemicals are in a sealed bulb and we identify the equilibrium condition with the so-called Helmholtz freeenergy function (denoted by the symbol A). The constant pressure case represents a reaction which is vented to the atmosphere and in this case the equilibrium condition is identified with the so-called Gibbs freeenergy (denoted by the symbol G). These are called thermodynamic potentials because when the changes of these properties are calculated to be less than zero, the chemical reaction may take place. If the changes of these functions are zero, then the system is in chemical equilibrium. As shown in the illustration on page 19 (Figure 7), changes in the nonequilibrium (script letters  $\mathcal{A}, \mathcal{A}$ ) potentials are always zero by our postulated equation. The Second Law is an integral part of the definition and we have not insisted, as is common in such proofs, that the temperature remain constant. In a chemical reaction the temperature may indeed return to its original value which signifies that a particular amount of heat transfer has taken place. Our proof is more general; we can admit any amount of heat transfer. Of course, dA and dG are still less than zero since they both equal &dT due to their equilibrium definition. The changes in the nonequilibrium thermodynamic potentials (A and A) do equal zero in a very straightforward way. The only work mode included here has been that

$$dE = d(\tau ) + \delta W$$

$$W = -pdV + \dots$$

$$dE = d(\tau ) - pdV + \dots$$

I. Constant Volume Case:  $dE = (\tau \lambda)$ 

So 
$$E - \tau S = constant$$
Let 
$$E - \tau S = Constant$$

$$\Delta E - \tau S = Cons$$

II. Constant Pressure Case: dE = d(τδ) - pdV

$$dE = d(\tau \mathbf{J} - pV)$$

$$d(E - \tau \mathbf{J} + pV) = 0$$
So 
$$E - \tau \mathbf{J} + pV = \text{constant}$$
Let 
$$E - \tau \mathbf{J} + pV = \mathbf{J} \text{ (Gibbs free-energy)}$$
Now 
$$dE = \delta Q + pdV$$

$$\delta Q - pdV = \tau d\mathbf{J} + \mathbf{J} d\tau - pdV$$

$$\delta Q - \tau d\mathbf{J} = \mathbf{J} d\tau \leq 0$$

$$\underline{\delta Q \leq \tau d\mathbf{J}}$$

(Script letters denote nonequilibrium parameters)

FIGURE 7

of expansion or compression but other work modes could have been taken care of in a similar fashion.

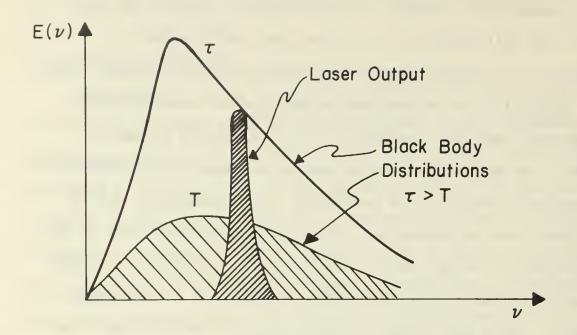
#### Electromagnetic Radiation

Electromagnetic radiation presents a particularly topical field in which to give an example. It was stated earlier that the fundamental particle for radiation is the photon. This particle has some very unusual properties which bear mention. First of all, photons do not follow a conservation of mass constraint; they are created or destroyed as energy increases or decreases, i.e., they obey the laws of momentum and energy only. Photons, moreover, do not interact with each other, which means that if two beams of light which are in phase crossed each other in a vacuum, there would be no effect on either one. Unless a photon interacts with matter, its fate is unchanged. Photons, of course, as waves do interfere with each other.

Now, supposing we have an enclosure made of perfectly reflecting walls which is evacuated creating a situation that is essentially a perfectly insulated container. We open a trap door and shine some radiation into this box. If the radiation comes from a source which temperature is higher than the walls of the box, after the trap door closes, there will be a nonequilibrium situation inside the box. As mentioned before, this is the case of the isolated system at nonequilibrium where any spontaneous change will in all probability increase the entropy of the radiation.

In order to accomplish the equilibration process we must introduce some absorbing material such as carbon dust which acts as a catalyzer. The "temperature" T will decrease and the entropy will increase. (In cases where the fundamental particles are not photons, collisions by the particles themselves would promptly cause the equilibration process to occur within the volume of the box; of course, this also happens at the walls.)

The situation of laser generated radiation is an interesting one from a thermodynamic viewpoint. We know that the energy of the laser beam is very well ordered (i.e., it has a very narrow spread in frequency -- it is coherent, meaning singly polarized and in phase). This order implies that the entropy must be very low and concurrently the "temperature" very high. Referring to the illustration on page 22 (Figure 8) we may see this from the equivalent black-body temperature of the spectral intensity of the laser beam. This "temperature" must be much higher than the temperature of the equilibrium distribution of the same quantity of energy. Hence, laser radiation is energy in a highly nonequilibrium state. But this is what we emphasized as the relevant feature of a work mode, namely, a narrow spread on the spectrum of the energy giving a high "temperature." It would be very difficult, for example, to discriminate laser radiation from black-body radiation at T = T which has been passed through a window corresponding to the frequency range of the laser radiation. But is the laser really a work mode for electromagnetic energy? We said at the introduction that work was premium energy. Witness the extensive laboratory utilization of laser radiation for optical measurements, welding, etc., etc. It is perhaps reminiscent of the impact of the use of electricity for power. In research work, lasers are now almost as essential as electronics. The classical way of finding out whether or not a certain energy mode in transit is work is to see if it raises a weight in a gravity field. Well, laser beams have done so [see "The Pressure of Laser Light," by A. Ashkin, Scientific American, February, 1972]. Laser light has already been used for propulsion and for the generation of ultrahigh temperatures.



For a fixed quantity of energy, the spread in the frequency ( $\nu$ ) is an index of the entropy content of the radiation, i.e., the larger the spread the greater the entropy. The black body spectrum represents the maximum entropy corresponding to a particularly prevalent distribution of the spectral energies over the entire frequency spectrum. The higher the black body temperature the more intense will the spectral component of the energy be. These spectral components propagate independent of one another because photons do not interact with each other.

FIGURE 8

### Conclusions

By giving a complete formulation of the Second Law which expresses energy in terms of entropy and temperature and relevant work modes, we have clarified the mysterious entropy inequality for nonequilibrium or irreversible cases. This, of course, has been done at the expense of introducing an extension of the concept of temperature, for which there is no further insight other than the fact that it always decreases as an isolated system approaches equilibrium. We note that temperature, pressure, and entropy change from their equilibrium value when the isolated system is at nonequilibrium, whereas energy must be conserved. The identification of the concept of temperature with the spectral distribution of energy links temperature to entropy, and has the attractive feature of describing the thermal work potential. The exact nature of this nonequilibrium "temperature" will probably be found from considerations of microscopic thermodynamics and once this nature is found, it must be consistent with Boltzmann's postulate for the entropy or the more general Gibb's statement. The fact that a nonequilibrium temperature may be defined is the key to the simplifications of the formulation of the Second Law presented in this article.

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(PAGE 1)

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